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Purification of FAME of *Jatropha curcas* by Acid-activated Bentonite Adsorption

(*Pemurnian Metil Ester Asam Lemak Jarak Pagar(Jatropha curcas) melalui Adsorpsi Menggunakan Bentonit yang Diaktivasi Asam*)

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abstract

Acid-activated Bentonite were used as adsorbents for purification of fatty acid methyl ester (FAME) of *Jatropha curcas* by adsorption method at atmospheric condition. Acid-activated Bentonite were prepared by aqueous impregnation technique. 5.3 M HCl and 40% by mass of H_2SO_4 were supported on bentonite by aqueous impregnation, washing with deionized water till Cl^{-1} and SO_4^{-2} ions were not detected, drying overnight and calcinated at 500 °C for three hours. Six methods for the purification step in biodiesel production were compared: (A) washing with distilled water at 50°C; (B) adsorption with bentonite; (C) adsorption with HCl-activated bentonite; (D) adsorption with HCl-activated bentonite and calcinated at 500 °C (E) adsorption with H_2SO_4-activated bentonite; (F) adsorption with H_2SO_4-activated bentonite and calcinated at 500 °C. The refining loss, methyl ester composition, ester loss and other properties, such as density, kinematic viscosity, water content, composition of catalyst and soap and pH were determined.

KEY WORDS: Biodiesel, *Jatropha curcas*, purification, adsorption, fatty acid methyl ester, FAME, acid-activated bentonite

abstrak

Bentonit yang diaktivasi asam digunakan sebagai adsorben pada pemurnian metil ester asam lemak jarak pagar *(Jatropha curcas)* menggunakan metode adsorpsi pada kondisi atmosfir. Bentonit yang diaktivasi asam disiapkan melalui teknik impregnasi cair. 5,3M HCl and 40% massa H_2SO_4 diimpregnasikan ke dalam bentonit, dicuci sampai tidak ada lagi sisa ion Cl^{-1} dan SO_4^{-2}, dikeringkan semalam dan dikalsinasi pada suhu 500 °C selama 3 jam. Tiga metode pemurnian pada produksi biodiesel dibandingkan: (A) pencucian dengan air distilata pada suhu 50°C; (B) adsorpsi menggunakan bentonit; (C) adsorpsi menggunakan bentonit yang diaktifasi dengan HCl; (iv) adsorpsi menggunakan bentonit yang diaktifasi dengan HCl dan dikalsinasi pada suhu 500 °C; (v) adsorpsi menggunakan bentonit yang diaktifasi dengan H_2SO_4; (vi) adsorpsi menggunakan bentonit yang diaktifasi dengan H_2SO_4 dan dikalsinasi pada suhu 500 °C Kehilangan selama pemurnian *(refining loss)*, komposisi metil ester, kehilangan ester dan sifat-sifat lain, seperti kerapatan, kekentalan kinematik, kadar air, kandungan sabun dan catalyst dan pH dianalisis.

Kata-kata kunci: Biodiesel. *Jatropha curcas*, pemurnian, adsorpsi, metil ester asam lemak, FAME, bentonit

INTRODUCTION

Biodiesel is defined as fatty acid methyl esters (FAME) derived from renewable feedstocks, such as vegetable oil, animal fats or waste cooking oil, used in compression ignition engine. The most commontly used method for preparing

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biodiesel is the transesterification reaction (Freedman et al 1984; Ma and Hanna 1999; Zou and Boocock 2006; He et al 2006, among many authors). Fat and oil react with alcohol (methanol and ethanol) to produce FAME or FA ethyl esters, namely, biodiesel, whose molecular sizes and properties similar to those of diesel fuel. Transesterification consist of three consecutive, reversible reactions: the TG is converted stepwise to DG, then MG, and finally glycerol, with methyl ester being formed in each step (Zhou and Boocock 2006).

Besides the main products (ester and glycerin), there are some impurities in the final products because of the existence of contaminants in the oil and incompleteness of the reaction. The present of minor contaminants can be detrimental to both engine and the environment (Karaosmanoglu et al 1996). The contaminants to be considered includes water, glycerin, alcohol, free fatty acid, soap and residual catalyst. The precence of contaminants will affect the properties of biodiesel (Gerpen et al 1996).

Current limits on the concentration of contaminants in biodiesel are set out in guidelines, such as those published by ASTM (Gerpen et al 2004 and He et al 2006). Purification step after transesterifications is necessary to decrease of the contaminants in order to fulfill the properties of biodiesel standard.

The purification of the transesterification reaction products brings an extra cost. The purity level of the biodiesel must conform to the standards for alternative diesel fuels. There are many methods for purification FAME, such as washing with hot distilled water, dissolving in petroleum ether and then washing with distilled water, and neutralization with H_2SO_4 (1:1). Among these methods, washing with hot distilled water at 50 ^oC was chosen as the best purification process (Karaosmanoglu et al 1996). He et al (2006) compared these traditional purification methods with the application of hollow fiber membrane in purification step. The densities, kinematic viscosities, water contents, acid values, methyl ester composition of purified FAME and ester losses were determined to evaluate the effectiveness of the purification methods. All these results show that washing with hot distilled water at 50 ^oC and the application of hollow fiber membrane are promising method for purification of biodiesel.

Washing biodiesel with hot water has limitation and environmentally weakness, because of using much water and energy. The application of hollow fiber membrane is technically difficult and brings an extra cost. In this study we tried to find an alternative method for purification of biodiesel by using bentonite as adsorbent. Bentonite has the potential to be used as low cost adsorbent since it is naturally available and has high surface area and their tendency to absorb water in the interlayer sites. These properties are enhanced with acid activation and treatment with organics Acid activation increases the surface area and modifies the structure of smectites. The extent of these changes depend on the acid strength and time of treatment (Babaki et al 2008).

Objectives

In this work, activation of bentonite has been considered for the removal of contaminants from FAME of *Jatropha curcas*. The main objectives were: (a) to determine the ability of physically and chemically activated bentonite to adsorb contaminants from biodiesel, (b) to compare the efficiency of treated bentonite to natural "untreated" bentonite and traditional method for the removal of contaminants, (c) to study the effect of different activation methods on the adsorption process.

MATERIAL AND METHOD

Materials

Jatropha curcas oil was hydrolic press extracted of jatropha seed from Lampung, South Sumatra, Indonesia. Anhydrous methanol (MeOH), 99.8%, potassium hydroxide (KOH), sulfuric acid (H_2SO_4), and Hydrochloric acid (HCl), 37-38% pure were purchased from ChemAR®.

A calcium-rich bentonite (CaB) sample was obtained as powder from PT. Superintending Company of Indonesia used in the experiments. The effects of calcinating and acid activation on some physicochemical properties of this material is being investigated **(Nazir, N. M.A. Yarmo, J. Salimon, and N. Ramli, *prepared for publication*)**. The bulk chemical analysis of the bentonite (mass %) is SiO_2, 64.15; TiO_2, 0.47; CrO_3, 0.003; Al_2O_3,.70; Fe_2O_3, 0.10; MgO, 0.70; CaO, 0.03; , Na_2O, 0.20; K_2O, 0.50 and loss on ignition (LOI), 22.61.

Preparation of crude FAME.

Crude FAME were prepared by esterification-transesterification reaction according to the method by Tiwari et al (2007). At a constant stirring rate (400 rpm), 200 ml of bentonite-bleached jatropha oil was pretreatment with methanol (0.28 v/v) using H_2SO_4 as catalyst (1.43% v/v) in 88-min reaction time at 60 °C temperature. After pretreatment, the product was used for the final alkali-catalyzed (3.5+acid value, w/v KOH) transesterification reaction with methanol (0.16 v/v) to produce biodiesel in 24 min of reaction time.

Acid activation of Bentonite

Acid-activated Bentonite were prepared by aqueous impregnation technique. 5.3 M HCl and 40% by mass of H_2SO_4 were supported on bentonite by aqueous impregnation (at 80 °C and 4 h), washing with deionized water till Cl^{-1} and SO_4^{-2} ions were not detected, drying overnight and calcinated at 500 °C for three hours.

Investigation of Biodiesel Purification by Different Methods

Six methods for the purification step in biodiesel production were compared: (A) washing with distilled water at 50°C. The washing process was carried out in water bath at 125 rpm for 20 minutes, and then ester and water phases were separated in separatory funnel. Wahing was carried out in 7 times; (B) adsorption with "untreated" bentonite; (C) adsorption with HCl-activated bentonite; (D) adsorption with HCl-activated bentonite and calcinated at 500 °C (E) adsorption with H_2SO_4-activated bentonite; (F) adsorption with H_2SO_4-activated bentonite and calcinated at 500 °C.

Each purification experiment was carried out in an open 400 mL beaker containing a stirred suspension of a 2% by mass bentonite in biodiesel oil. The mixture was then heated to 80°C, kept at this temperature interval for 20 min. The oil was then filtered through Whatman No. 41 filter paper.

Analysis of methyl esters

The FFA content of FAME was determined by titration with standard 0.01 N NaOH solution. The color index of biodiesel was determined by using a *Lovibond Automatic Tintometer Model F (The Lovibond Limited, UK)*. pH of biodiesel was determined by using *Standard pH-meter PHM 210 (MeterLab®-Radiometer Villeurbanne Cedex, France)* and density was determined by picnometer method. The visvosity of biodiesel was determined using *Digital Viscometer Model DV-I Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA.* (spindle 3, 100 rpm). Water content was determined by heating the biodiesel using oven (104°C, 30 minutes) The amount of soap and residual catalyst in biodiesel was determined by adding a sample to a larger quantity of aceton and titrating with 0.01N HCl using phenolphtalein indicator (for residual catalyst measurement) and bromophenol blue indicator (for soap measurement)(Gerpen et al 2004). Fatty acid methyl ester composition was analysed using *Shimadzu-GC17A Gas Chromatograph, Japan.* Ester loss was determined based on method by Ma and Hanna (1999) and He et al (2006).

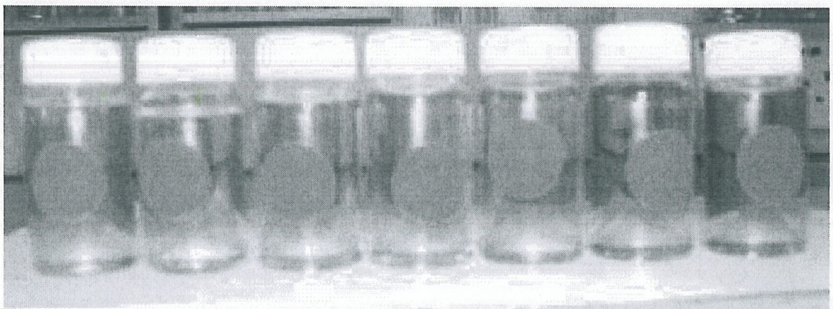
RESULT AND DISCUSSION

Effect of Purification methods on Color

Results showed that the use of acid-activated bentonite corresponded to the increase of color scale. Washing the biodiesel with hot water (A) decreased color scale of biodiesel (Figure 1).

Effect of Purification methods on Physico-chemical properties

After the transesterification reaction is complete, the leftover catalyst and soap tend to concentrate in the glycerol phase. However, some soap and a small amount of catalyst may be left in the biodiesel phase (Gerpen et al 2004). Knowing the amount of soap formed and catalyst resides is useful to see how effective the purification in the removing these two compounds.



Treatment	Control	A	B	C	D	E	F
Yellow color index	1,4	1.1	1.3	1.8	2.3	2.8	3.4

Figure 1. Color variability of purified biodiesel

Table 1 shows that there was no resisual catalyst detected in biodiesel, whether it was in control (A) or in purified biodiesel (A-F). There was 0.099% soap was detected in unpurified biodiesel and soap was not detected in purified biodiesel for all purification method. All purification methods are suitable to adsorb the soap contaminant.

The density of biodiesel for all purifying method was not significantly different.

Table 1. Physico chemical properties of purified biodiesel

	Treatments						
Property	Control	A	B	C	D	E	F
Catalyst (%)	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Soap (%)	0,099	n.d	n.d	n.d	n.d	n.d	n.d
Density (g/cm^3)	0,86	0,87	0,87	0,87	0,87	0,87	0,87

*) *n.d (not detected)*

Results of the kinematic viscosity indicated that there was significant difference among the treatments. Purification with hot distilled water (A) indicated the smallest figure and purification with bentonite increased the viscosity of biodiesel (Figure 2a). The result indicated that all purified biodiesel fulfill the ASTM standard of kinematic viscosity (6,0 mm^2/s, maximum).

Purification methods decreased the pH (Figure 2 b). Washing with hot water (A) increases the water content of biodiesel and purification with bentonite decrease the water content (Figure 2c). The treatments indicated that all purified biodiesel was not fulfill the ASTM standard of water content (0.1 %).

The results on Figure 2d show that the refining loss increase with the increasing of the acidity the bentonite.

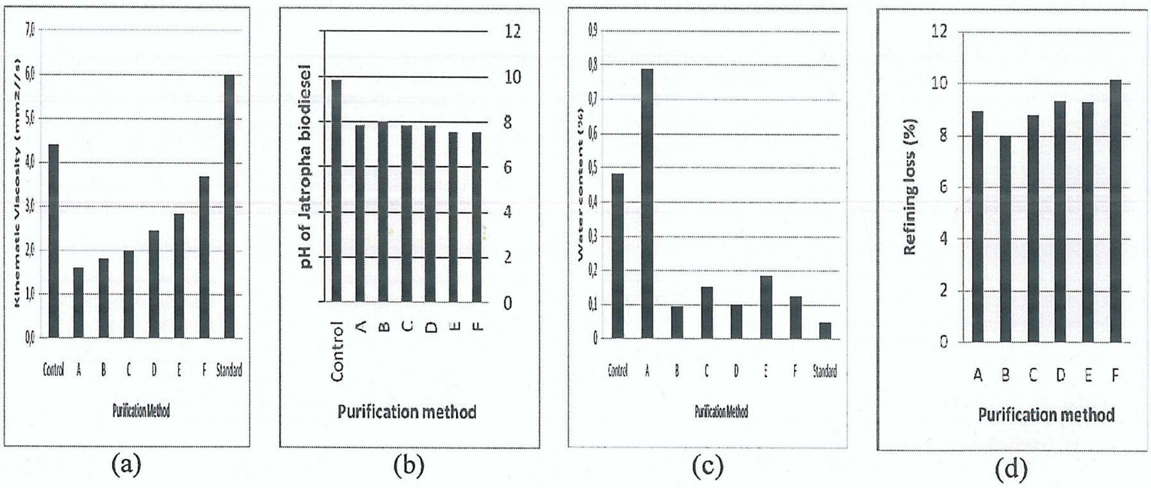


Figure 2. Effect of Purification methods on kinematic viscosity (a), pH (b), Water content (c) and Refining loss (d) of biodiesel

Effect of Purification methods on methyl ester composition

The results on Table 2 show methyl ester distribution of purified jatropha biodiesel. Figure 3 shows that the fatty acid components were not significantly different between "unpurified biodiesel" and "purified biodiesel".

Saturated and unsaturated ratio of all purification methods were not significantly different (Figure 4a). Ester loss increase with the increasing of acidity (Figure 4b). Bentonite purification (ester loss = 8.1%) in this study is better than convensional method by Hu et al (2006) and similar to purification using hollow fiber membrane.

Table 2. Effect of purification method on Fatty acid present in *J. curcas* biodiesel (wt%)

Acid Common Name	**Structure**	Purification methods						
		Control	A	B	C	D	E	F
Palmitic	C16:0	14,07	13,65	14,34	14,12	14,10	14,10	14,07
Palmitoleic	C16:1	0,94	1,01	0,98	0,99	1,00	1,00	0,90
Stearic	C18:0	6,03	5,50	5,24	5,23	5,07	5,15	5,35
Oleic	C18:1	43,55	44,19	44,20	44,01	44,17	43,96	43,65
Linoleic	C18:2	34,50	33,54	34,16	34,50	34,31	34,31	34,01

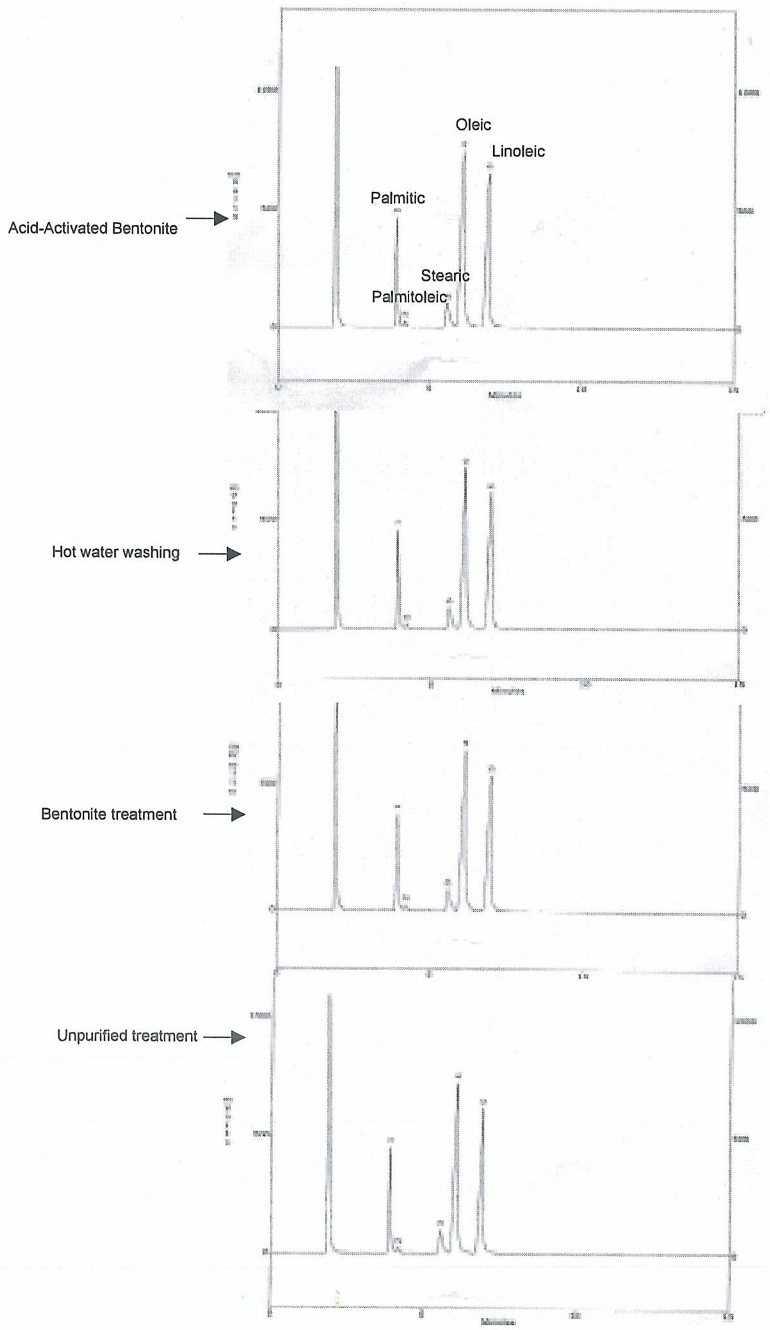


Figure 3. Chromatograms fatty acid composition from different purification method

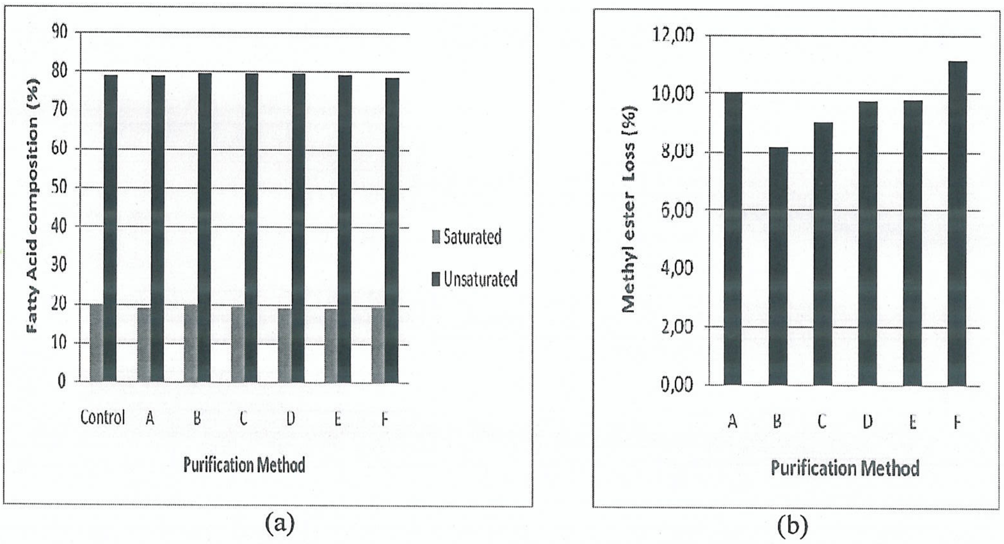


Figure 4. Effect of Purification methods on saturated and unsaturated composition (a) and Ester loss (b)

CONCLUSION

Based on the objectives of this study we can conclude as follow:
(a) Bentonite has an ability of phisically and chemically to adsorb contaminants from biodiesel (b) Saturated and unsaturated ratio of all purification methods were not significantly different. Color index, refining loss, kinematic viscosity, the ester loss increase with the increasing of acidity of bentonite adsorbent (c) Purification of biodiesel with bentonite without treatment is the best purification method. Hence the acid activation of bentonite before adsorption is not required.

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